ABSTRACT

CHEMISTRY

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SURFACTANT ENHANCED EXTRACTION OF PCBs FROM SOILS

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The soil utilized in surfactant enhanced extraction of polychlorinated biphenyls (PCBs) from soils was determined to have low cation exchange capacity, low total organic content, and be of a sandy nature. PCBs spiked onto the soil obtained from the Savannah River Site (SRS) were distributed according to particle sizes. The smaller the particle fraction, the higher the surface area and the higher the PCB loading. Anionic or neutral surfactants and combinations thereof showed various degrees of effectiveness in extracting PCBs from the soil, based on the surfactant type and their critical micelle concentration (CMC). On equivalent CMC basis, sodium dodecylsulfate (SDS), 1-dodecylpyridinium chloride (1-DPC), Witconol SN-70 and Igepal CA 720 were most effective in extracting PCBs from the 100 ppm spiked SRS soil. Further studies with Witconol SN 70, an alcohol ethoxylate surfactant, shows that using a 0.5 wt % surfactant solution, 50% of PCBs was removed from 100 mg/kg spiked soil within 24 h, at 25^0C, whereas, with a 5 wt % solution, 100% of the PCBs was removed. Modification of the pH of the soil-surfactant slurry slightly increases PCBs extraction, whereas the addition of inorganic electrolytes and small molecular weight alcohols caused a significant reduction in the surfactant extraction efficiency.

SURFACTANT ENHANCED EXTRACTION OF PCBs FROM SOILS

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CHAPTER 1

INTRODUCTION AND STATEMENT OF THE PROBLEM

1.1 Introduction

Polychlorinated biphenyls (PCBs) are a group of relatively persistent, ubiquitous and highly carcinogenic environmental contaminants.[1] Although they have plagued the environment for many years, it was not until the 1970s that the extent of their potential health effects sparked great concern. The impact of their existence has been so significant that billions of dollars have been spent by governments and private organizations for environmental remediation of these highly chlorinated compounds. Three major worldwide contamination incidents have gained much attention, namely, the Yusho incident in Japan, the Hudson River in New York and New Bedford Harbor in Massachusetts.[2] Finding effective scientific approaches to decontaminate PCB containing soils and sediments poses a major environmental challenge. This project investigated the effectiveness of surface active agents (surfactants) for the removal of PCBs from contaminated soil.

1.2 PCBs in the Environment

Since their formulation in the 1920s, PCBs were extensively used because of their outstanding physical and chemical properties. They were used in capacitors, transformers, and compressors due to their excellent dielectric properties. They were also used in plasticizers, hydraulic fluids, lubricants, coolants, sealants, lacquers, inks, paints, pesticides, carbonless copy paper, and components of paint. Their resistance to oxidation, acids, bases, and other chemical agents resulted in their use as thermal stabilizers. Between 1930 and 1977, 5.67 x 10^9 kg of PCBs were produced by the Monsanto Company in the United States.[2]

The widespread use of PCBs over the years has resulted in severe environmental contamination. In some instances, they were reported as being splashed on unpaved roads to reduce dust.[3] It is reported that PCBs were disposed of directly in rivers, lakes, streams, and municipal landfills during the late 1920s through the mid 1970s.[2] PCBs were also released into the environment by atmospheric emissions resulting from insufficiently capped landfills. It has been estimated that up to 8 x 10^8 kg of PCBs have been dumped directly into the environment. Many fisheries have been closed as a result of the hazard of eating PCBs contaminated fish.[2] In 1995, the EPA estimated that 26 million cubic yards of soil on the U.S. National Priority List of sites were contaminated.

Since then, several studies have shown that PCBs are potential carcinogens and readily concentrate in human and animal tissues. PCBs are lipophilic, meaning they have an affinity for oils or fatty tissue. When the knowledge of their carcinogenic nature surfaced, the soil in several landfills were excavated and placed in EPA approved landfills. Despite the removal of the PCB-laden soil, there still exist contamination well above the EPA allowed limit of 2 mg/kg.

Of specific interest to this research project was the widespread PCB contamination at several Department of Energy complexes across the United States, and in particular, the Savannah River Site (SRS) in Aiken, S.C. PCBs exist at numerous DOE sites as components of their hazardous wastes and mixed wastes.

1.3 Objective

The objective of this project was to investigate the use of surfactants to enhance the extraction of PCBs from soil.

1.4 Approach to Research

This research project focused on the application of surfactants to enhance the extraction of PCBs from the soil. Characterization studies were performed on soil from the Savannah River Site to provide information about its physico-chemical properties such as total organic carbon, cation exchange capacity, pH, surface area, percent dry weight, and particle size distribution. The PCB-free soil was spiked with Aroclor 1254, a blend of PCB congeners, and extracted with various types of surfactants. A general screening was performed on the surfactants to provide an indication of their relative efficiency in removing the PCB from soil. A model surfactant was selected from among the most promising for further soil-washing studies. The model surfactant was characterized for its critical micellar concentration (CMC) and its capacity to solubilize PCBs. The surfactant was further investigated for its effect on desorbing PCBs from soil as a function of various parameters, including surfactant concentration, organic and electrolyte additives, temperature, time, and pH.

CHAPTER 2

LITERATURE SURVEY

2.1 Nomenclature and Characteristics of PCBs

Polychlorinated biphenyls are viscous, odorless, mostly colorless, aromatic compounds with one to ten chlorine atoms arranged about two attached benzene rings. There are 209 possible arrangements, with each denoting a congener. According to the International Union of Pure and Applied Chemists, each congener is assigned a number between 1 and 209. Each congener has its own unique chemical structure (specific number and arrangement of chlorine atoms).

In past commercial practice, manufacturers sold PCBs as a combination of several congeners under a specific trade name. In the U.S., the Monsanto company, the largest manufacturer of PCBs marketed its congeners as aroclors. Each group was termed Aroclor, and given a four digit numerical name. The first two digits denote the number of carbon atoms in the compound, and the last two digits denote the average chlorine content by weight.[2] For example in Aroclor 1254, there are 12 carbon atoms and an average 54% chlorine by weight.[3] Figure 1.2 gives an example of two congeners found in Aroclor 1242.

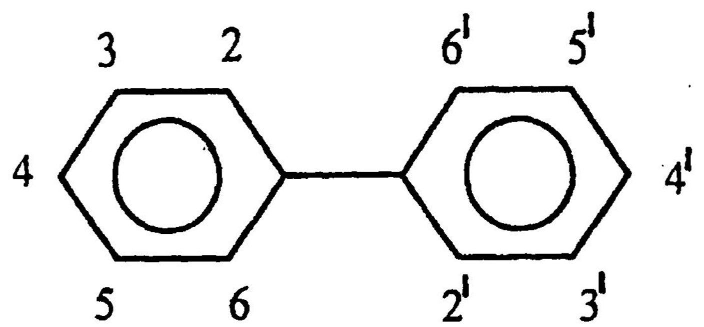
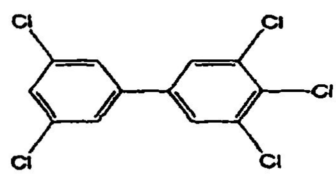
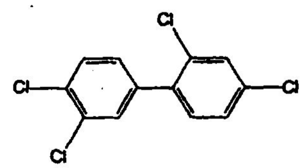


Figure 1.1: The Chemical Structure of a PCB Molecule with Possible Chlorine Positions





2,5,3',4',5' penta-chlorobiphenyl

4,5,4'6' tetra-chlorobiphenyl

Figure 1.2: Two Congeners found in Aroclor 1242

2.2 The Transport and Fate of PCBs in the Environment

PCBs have low aqueous solubility. For example, the aqueous solubility of AR 1254 has been found to be 40 μg/L.[2] They are soluble in most organic oils and fats. They do not degrade readily in the environment. PCBs have an affinity for nonpolar phases and tend to adhere to the organic portion of the soil particles. They bind to the intercrystalline layers of montmorillonite clay particles. Because PCBs are very large molecules and have low solubility, they migrate slowly through soil and in water, less than a few centimeters a year.[4]

2.3 Approaches to PCB Remediation

Several technologies have been developed and in several cases implemented towards the remediation of PCBs. Among these are chemical dechlorination, pump and treat (for aqueous contamination), land excavation/dredging, and soil washing. Reductive dechlorination is very effective in reducing the toxicity of PCBs.[5] It has been reported that under reducing conditions, anaerobic communities can dechlorinate PCBs at a rate of up to 3 μg Cl/g sediment/week at 12° C for PCBs concentrations ranging from 100 to 1000 mg/kg.[9] Pump and treat remediation was initially utilized for the cleanup of both organic and inorganic contaminants in contaminated groundwater.[6] However, in recent years, the limitations of this approach has been recognized. One of the drawbacks encountered using this technology is the extended time required to reach acceptable cleanup levels.[7] Another is that the amount of organic contaminant that may be retained in the soil has been reported to range from 10% to 50%.

Soil washing uses water and mechanical scrubbing and has been imported from the mining industry for environmental remediation. With this technology, PCBs can be either dissolved or suspended in a wash solution for subsequent wastewater treatment or concentrated into a smaller volume by particle size separation, since the PCBs tend to preferentially adsorb to the fine clay and silt particles. Fullscale application can be quite complex with multiple unit processes. The water wash solution may be augmented with acid or bases for pH adjustment, as well as detergents, surfactants, coagulants, and flocculants.[3]

2.3.1 Solvent Extraction of PCBs

Commercial processes for the extraction of PCBs are few. Meckes et al. reported that triethylamine (TEA) solvent extraction of PCBs from river sediments using Resources Conservation Company's Basic Extractive Sludge Treatment (B.E.S.T) process showed 99% removal of PCBs, and extraction efficiency remained high regardless of congener class.[8] A site demonstration of Terra-Kleen Response Group's mobile solvent extraction process reported a 98.8% removal of 144 mg/kg of PCBs from contaminated soil over 11 extraction cycles using a proprietory solvent. The process was reported to be very effective in soil decontamination of PCBs.[9]

Other processes for PCB extraction are at the bench scale. PCB extraction by supercritical fluid extraction (SFE) was reported to be a potentially attractive alternative to solvent extraction. Morselli et al. reported a 92% removal efficiency of PCBs by supercritical fluid extraction of soils and sediments on a bench scale.[10] Zappoli et al. investigated the use of methylene chloride as a solvent for PCB extraction. The extraction efficiency was affected by dissolved organic matter content and soil/sediment pH.[11] Brown et al. reported that treatment of PCB containing low-level mixed waste (solid waste and sludge) using supercritical carbon dioxide extraction as a promising technology.[12] This technology was also investigated by Schulz et al. who reported that SFE reduced PCBs levels in soil to less than 1 mg/kg.[13]

2.4 Surfactants and Their Uses in PCB Extraction

2.4.1 General Surfactant Characteristics

Surfactants are surface active agents having two distinct moieties or regions: hydrophilic polar head group and hydrophobic nonpolar tail.[14] In aqueous organic media, the molecules migrate to the interface where both the regions are in a preferred phase, which then causes the surfactants to accumulate at different interfaces (e.g. air-water, oil-water).[20] At certain concentrations in aqueous solution, surfactants position themselves into circular masses called aggregates, with the hydrophobic portion of the molecule in the interior of the aggregate and the hydrophilic portion extended into the aqueous phase. The aggregates are commonly called micelles (Figure 2.3), and the concentration of the surfactant at which micelles are formed is called the critical micelle concentration.[15]

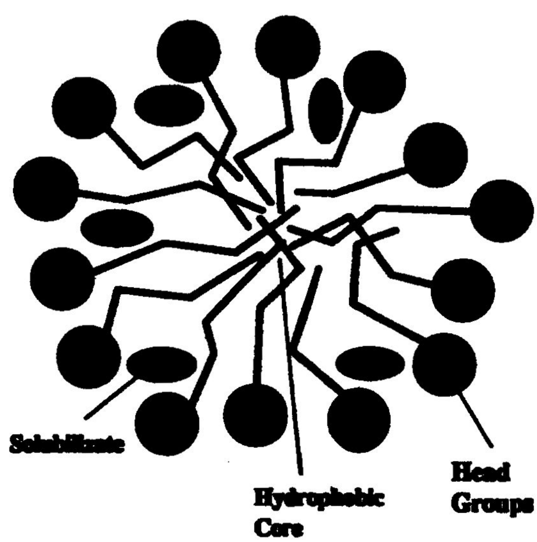


Figure 2.3: Representation of a Micelle

Surfactants can improve subsurface remediation by increasing the solubilization of the hydrophobic contaminant. In this manner, solubilization is simply the process by which the aqueous phase concentration of contaminants is increased due to the partitioning or separation into surfactant micelles.[16] Solubilization enhancement is the result of the partitioning of the contaminant into the oil-like core of the micelle, thereby increasing the solubility of the contaminant and decreasing the time required for its extraction from the soil or subsurface.[9]

2.4.2 Types

Commercial surfactants are available in four types: anionic, cationic zwitterionic, and nonionic.[16] Examples are given below.

1. *Anionic:* The surface-active portion of the molecule bears a negative charge, e.g., $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate);
2. *Cationic:* The surface-active portion bears a positive charge, e.g., quarternary ammonium chloride $RN(CH_3)_3^+Cl^-$ (salt of a long-chain amine);
3. *Zwitterionic:* both positive and negative charges may be present in the surface active portion, e.g., $RN^+H_2CH_2COO^-$ (long-chain amino acid);
4. *Nonionic:* The surface-active portion bears no apparent ionic charge, e.g., $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid).

2.4.3 Surfactant Solubilization and Surfactant Remediation

The interior of a micelle consists of nonpolar hydrocarbon chains, that have the ability to dissolve large quantities of nonpolar solutes that are virtually insoluble in aqueous phases due to increased partitioning or separation into micelles.[17] Below the surfactant critical micelle concentration, solubilization does not occur.[20] However, above the CMC, the amount of solute dissolved is approximately a linear function of the surfactant concentration. Solubilization is believed to occur at numerous positions on the

the CMC, the amount of solute dissolved is approximately a linear function of the surfactant concentration. Solubilization is believed to occur at numerous positions on the micelle: (1) at the micelle solvent interface; (2) between the hydrophilic head group; (3) in the palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms that comprise the outer core of the micellar interior; (4) more deeply in the palisade layer; and (5) in the inner core of the micelle.[16]

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Approach

The "PCB-free" soil used in this project was obtained from Savannah River Site, Aiken, SC. The soil was chosen such that it was of similar physicochemical characteristics to areas on the site that were contaminated with PCBs.

Characterization studies were performed on soil to provide information about the nature of the soil (such as total organic carbon, cation exchange capacity, pH, surface area, and percent dry weight). The soil was chosen because it was environmentally safe and could be transported without federal regulation. Sieve analysis was conducted to determine the particle size distribution of the soil. The soil was loaded with PCB Aroclor 1254, and a general screening was performed using various surfactants to provide an indication of the efficiency of the surfactants' ability to solubilize PCBs. The addition of organic additives and electrolytes were incorporated in surfactant solutions at various concentrations to ascertain their effect on surfactant solubilization of PCBs. Temperature and pH were other parameters investigated for their effects in surfactant solubilization of the PCBs.

3.1.1 Materials and Apparatus

PCB free soil (Savannah River Site); *Surfactants*: Dodecyl sulfate sodium salt (Aldrich), Triton X-100 (LabChem), Brij 30 (Aldrich), Igepal CA-720 (Aldrich), Witcodet 100 (Witco Corp.), Witcolate D51-51, Witconol SN-70, Dodecylethyl-dimethylammonium bromide, 1-dodecylpyridinium chloride hydrate (Aldrich), Alcodet HSC-1000 (Rhone-Poulenc); *Internal Standard:* Pentachloronitrobenzene (Accustandard); *Surrogates:*Decachlorobiphenyl, Tetrachloro-*m*-xylene (Accustandard); *Water*: 18 MΩ deionized; *Solvents*: Hexanes (Fisher), alcohols: isopropanol, methanol, butanol, ethanol (Fisher); *Electrolytes:* KNO_3, $NaNO_3$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, NaCl, Na_2SO_4, (Fisher); *Syringes*: 5 μl, 10 μl, 25 μl, 50 μl, 100 μl, 250 μl, 500 μl; pH Buffers: 4, 7, 10 (Fisher) *Apparatus*: Burrell Wrist Action Shaker, Kuderna Danish Apparatus, Mechanical Rotator, Water Bath, 24/40 Concentrator tubes, AR 25 pH meter (Accumet), 125 mL Erlenmeyer Flasks, 40 mL environmental amber vials, HP autosampler vials, pastuerize pipettes, volumetric flasks, beakers, centrifuge vials, IEC centifuge, TCLP jars, ENVI Solid Phase Extraction Disks, sulfuric acid. *Instrumentation:* HP 5890 Gas Chromatograph/ECD Detector, Branson Ultra Sonicator, Gemini 2360 Surface Area Analyzer; Sieves:ASTM certified U.S.A. Standard Sieves.

3.2 Soil Quality Parameters

3.2.1 Sieve Analysis

A sieve analysis was performed by shaking the soil through a stack of 2 in. depth sieves with openings of the following sizes: #200 (75μm), #140 (106μm), #60 (250μm), #40 (425μm), #20 (850μm), #10 (2.00 mm), and #4 (4.75 mm).

A homogenized portion of the soil (500 g) was selected by the system of quartering. The sieves were stacked in order of decreasing mesh size and the pan placed on the bottom. The soil was sieved mechanically in a horizontal motion for at least 10 min. Each sieve and pan was weighed. The weights of the empty sieves and pan were subtracted from their weights with soil.

3.2.2 Cation Exchange Capacity for Soils (Sodium Acetate Method)

A 1-N sodium acetate solution was prepared by dissolving 136 g of $NaC_2H_2O_2 \bullet 3H_2O$ in water and diluted to 1 L. The pH of this solution was adjusted to 8.2 using 1N NaOH. A 1 N ammonium acetate solution was prepared by diluting 114 mL of glacial acetic acid (99.5%) with water to 1 L. A 138 mL aliquot of concentrated NH_4OH was added to water to obtain a volume of about 1,138 mL. The pH of the resulting solution was checked and additional NH_4OH was added as needed to adjust the pH to 7. The solution was then diluted to a volume of 2 L with water. Four grams of soil was transferred to a 50- mL, round bottom, narrow neck centrifuge tube. Thirty-three mL of 1 N sodium acetate solution was added, the tube was stoppered, vortexed for 5 min and centrifuged until the supernatant liquid became clear. The process was repeated. Using 99% isopropyl alcohol and ammonium acetate solution, the washing for each was decanted into a 100-mL volumetric flask. The combined washings were diluted to the 100-mL mark with ammonium acetate solution. The concentration of displaced sodium was determined by Inductively Coupled Plasma Mass Spectroscopy.

3.2.3 Percent Dry Weight

An aliquot of soil was added to a pre-weighed crucible and their combined weights were recorded. The soil was allowed to dry overnight in an oven at 105°C, cooled and was reweighed.

3.2.4 Surface Area Analysis

Approximately ½ inch of the soil was placed into a surface area tube, weighed and purged with nitrogen gas flow for 2 h at 200°C. The tube was then cooled to room temperature, weighed, and placed in a liquid nitrogen dewar in the surface area unit. The sample was evacuated and adsorption measurement performed at liquid nitrogen temperature using nitrogen as the adsorbate, using Gemini 2390 Surface Area Analyzer. The multipoint surface area was calculated using the Brunauer-Emmett-Teller (BET) equation.[18]

3.2.5 Total Organic Carbon Analysis

The total organic carbon was determined by ASTM 2974-87 at Hygeia Laboratories, Inc., Marietta, GA. This method uses the percent ash content to determine the total organic carbon. The moisture content was determined by drying the sample for 16 h at 105 °C or until there was no change in the mass of the sample after further drying periods in excess of one hour. Then the moisture content was determined in the following manner:

% Moisture Content =[(A-B) x 100]/A

where,

A = initial mass of the sample (g),

and

B = mass of the oven-dried sample

For ash content determination, a sample of the oven-dried soil was placed in the sample container and the mass of the container and specimen determined. The container was placed in a muffle furnace, the temperature gradually brought to 440 °C and held until the specimen was completely ashed. The specimen was cooled and the mass was determined. The ash content was determined as follows:

% Ash Content =(Cx100)/B

where,

C = weight of ash (g) and

B = weight of oven-dried test specimen, (g)

The organic matter was determined by the difference as follows:

% Organic matter =100.0-D

where D =ash content

3.2.6 Soil pH Measurement

A 20 mL portion of reagent water was added to 20 g of soil in a 50 mL beaker. The suspension was continuously stirred for 5 min. The soil suspension stood for about 1 h to allow most of the suspended clay to settle out from the suspension. The suspension was centrifuged to separate the aqueous phase for pH measurement.

3.3 Spiking Soil with PCBs

A one gram aliquot of PCBs mixture with tradename "Aroclor 1254" was weighed and dissolved in 1L of hexane in a 1L volumetric flask to give final concentration of 1000 mg/L. A 1.5 kg quantity of soil was placed in a 2 L TCLP jar and 150 mL of the AR 1254 solution was added. The soil/hexane slurry was rotated for 46 h on a TCLP mechanical rotator. The slurry was transferred to a clean desiccator, placed under a fume hood and with frequent stirring, the solvent was allowed to evaporate, leaving a fairly dry soil residue. The PCBs laden soil was safely stored in a large, covered dessicator.

3.3.1 Determination of PCB Concentration of Spiked Soil

The PCB concentrations in the overall (bulk) spiked soil and in various particle size fractions were determined by GC/ECD. For the bulk soil analysis 10 g of soil was used, whereas for PCBs analysis in the various size fractions, the bulk soil was mechanically sieved. Two grams of soil was taken from each sieve size. Each soil sample was placed in a small extraction thimble and 300 mL of a 1:1 hexane/acetone mixture was placed in a 500 mL round bottom flask. The samples were allowed to reflux for 16-24 h at 4-6 cycles/hr after which the extracts were cooled. The extracts were concentrated in 500 mL Kuderna-Danish concentrator fitted with a 10 mL collection tube, 1 μL of pentachloronitrobenzene was added to each as internal standard and the samples analyzed by GC/ECD under the conditions given in section 3.5. The extractions were performed in duplicates.

3.4 Preparation of Standards and Surrogates

In accordance with the EPA SW 846 Method 8082[19], the internal standard chosen was pentachloronitrobenzene (PCNB) prepared at 2.5 mg/L. The calibration standards were 1, 2, 5, 10, 25, 50, and 100 mg/L Aroclor 1254. They were prepared from a 1000 mg/L Aroclor 1254 standard and were each spiked with PCNB at 2.5 mg/L.

3.5 Analysis of Aroclor 1254

Detection and quantitation of PCB components are best achieved by using an Electron Capture Detector (ECD). The ECD has a distinct advantage for PCB analysis over other common detectors such as Thermal Conductivity Detectors and Flame Ionization Detectors since it is highly selective and sensitive for chlorinated compounds. The process of detection is based on electrons produced from ^{63}Ni radioactive source being captured by the high affinity chlorinated species. The higher the concentration of the chlorinated compound, the greater the amount of electrons captured.

GC-ECD quantitation is usually done by internal or external calibration method with the former being more accurate. With the internal standard method, the concentration of a particular compound in the sample is determined relative to a known standard. A calibration curve is determined by plotting the area ratio versus the concentration ratio, and the slope representing the average calibration factor, CF. The CF is used to calculate the sample concentration in the extract using the following equation:

$$CF = \frac{ADYZ}{BCZ'}$$

where, A is the concentration of the calibration standard, B is the concentration of the internal standard in the calibration standard, C is the area of the calibration standard, D is the area of the internal standard in the sample, Y is the concentration of the internal standard in the sample, Z is the area of the sample, and Z' is the area of the internal standard in the calibration standard.

In accordance with EPA SW846 Method 8082, GC/ECD analysis was conducted on an autosampler equipped, Hewlett Packard 5890 Series II Gas Chromatograph using the following conditions: Column HP-5/30M x 0.32 mm I.D. x 0.25 μm film thickness; Injector temperature-250 ^{0}C; Detector temperature-275 ^{0}C; Column initial temperature/time-140 ^{0}C/1 min., heating rate –12 ^{0}C/min to 190 ^{0}C for 2 min., then 4 ^{0}C/min., to 275 ^{0}C. Quantitative analysis was done by internal standard method. The summed areas of six consistent peaks in the chromatogram of each standard were ratioed with the area of the internal standard. The retention times of these peaks are presented in

Table 3.1. All calculations were done by the HP chemstation software. Figure 3.1 is a typical chromatogram of AR 1254.

Table 3.1: Retention Times of Chromatogram Peaks Used in the Quantitation of AR 1254

Peak ID	RT(min)
Internal Std. (PCNB) Peak	6.99
AR1254 Peaks:	
1.	11.7
2.	12.5
3.	13.9
4.	14.5
5.	16.0
6.	17.1

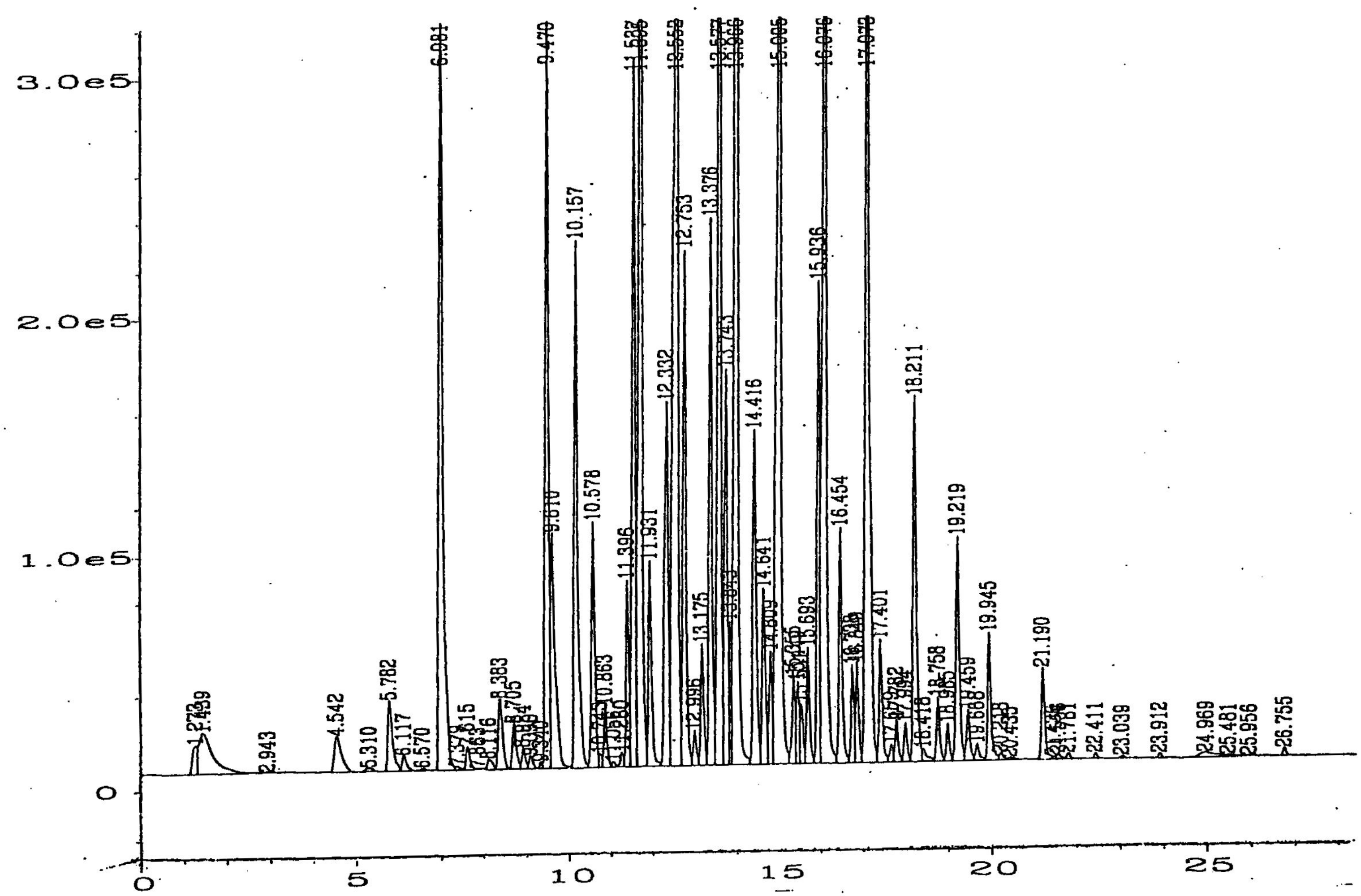


Figure 3.1: Chromatogram of Aroclor 1254

3.6 Studies on the Recovery of PCBs from Various Surfactant Solutions

Clean 125 mL Erlenmeyer flasks were spiked with 500 μL of 100 ppm AR1254. The contents were gently blown down with a small stream of dry nitrogen under a fume hood. Twenty-five mL aliquots of the surfactant solutions were placed in each flask and shaken for 24 h. The solutions were transferred to 40 mL amber vials, where they were extracted twice with 5 mL of hexane. The solutions were allowed to settle and a few drops of 2-propanol was placed in each vial to facilitate the separation of phases. Fifty μL of PCNB was placed in the 10 mL of hexane extract and one mL of the extract was analyzed by GC/ECD as per Section 3.5. Table 3.2 shows the surfactants type and concentrations investigated. The recovery studies were performed in duplicates and in some cases triplicates.

3.7 Determination of PCB Residue in Extraction Flasks After Surfactant Treatment

After drying, the Erlenmeyer flasks, which contained the surfactant solutions used in the recovery studies, were extracted twice with 5 mL of hexane to assess the amount of undissolved aroclor.

Table 3.2: Surfactants and Their Concentrations Used in Recovery Studies

Surfactant	Formula/Class	CMC (mg/L)	Recovery Concentrations		
			CMC	5xCMC	10xCMC
SDS	$CH_3(CH_2)_{11}OSO_3Na$	1.2×10^{-2}	x	x	x
1-DPC	$C_{12}H_{25}Pyr^+Cl^-$	1.7×10^{-2}	x	ND	x
Igepal CA 720	$4\text{-}(C_8H_{17})C_6H_4O(CH_2CH_2O)_{11}CH_2CH_2OH$	3.7×10^{-4}	ND	ND	x
Triton X 100	*p-t* $C_8H_{17}C_6H_4O(C_2H_4O)_{10}H$	1.7×10^{-4}	ND	x	x
Witcodet 100	Alkylbenzene Sulfonate/ Alcohol Ethoxylate	N/A	x	x	ND
Alcodet HSC 1000	Thioethoxylate	N/A	x	ND	ND
Witconol SN-70	$C_{10}\text{-}C_{12}O(C_2H_4O)_7H$	0.05 wt%	x	x	x
Witcolate D51-51	Alkyl Phenoxyether Sulfate	3.4×10^{-2}	x	x	ND
DDAB	$CH_3(CH_2)_{11}N(C_2H_5)(CH_3)_2Br$	1.6×10^{-2}	ND	ND	ND
Brij 30	$C_{12}H_{25}(OCH_2CH_2)_4OH$	2.3×10^{-5}	x	x	ND
Deionized Water	N/A	N/A	N/A	N/A	N/A

N/A= Not Applicable

ND= Not Done

3.8 Soil Extraction Protocol

The surfactants listed in Table 3.2 were prepared at multiple concentrations of their critical micelle concentration (CMC). Surfactants for which chemical information was proprietory were prepared as 0.5% (w/v) solutions. The pH of each surfactant solution was taken before and after agitation. PCB loaded soil was treated with each surfactant solutions as follows: Two grams of soil and 25 mL of surfactant solution were placed in a 125 mL Erlenmeyer flask, each flask containing a different surfactant. A control was included, which contained 2 g of soil and 25 mL of deionized water. The samples were agitated for 24 h using a Burrell Wrist Action Shaker, then samples were centrifuged at 2550 rpm for 15 min. The liquid was decanted, placed in a 40 mL amber vial and analyzed as per Section 3.5. The residual solids were retained for percent dry weight and for PCBs analysis.

3.9 Analysis of Residual PCBs in Soils After Surfactant Treatment

The soil samples were allowed to dry completely overnight under a fume hood and their dry weights recorded. The dried samples were extracted by ultrasonic extraction. Each sample was placed in a 20-mL beaker and 10 mL of a 1:1 hexane: acetone solution was added. The soil-solvent mixture was subjected to ultrasonic extraction for 2 min using a Branson Ultrasonic Extractor in pulsed mode at an amplitude of 65%. The samples were then filtered through a pasteurized pipette stopped with glass wool, into a 10-mL concentrator tube. They were then concentrated to 2 mL using the nitrogen blowdown technique, 1 mL of internal standard added, then reconcentrated to 2.0 mL. The extracts were cleaned-up by adding 5.0 ml 1:1 solution sulfuric acid and allowed to stand to complete phase separation. The organic layer was then siphoned. The PCB content in the samples was analyzed by GC/ECD as per Section 3.5.

3.10 Characterization of Witconol SN-70

3.10.1 Determination of CMC Using Surface Tension

The CMC of Witconol SN-70 was determined by using the surface tension method. The method is based on the principle that surface tension is proportional to the replacement of molecules of solvent at the interface by molecules of surfactant.

A 2% stock solution of Witconol SN-70 was prepared by dissolving 20 g of surfactant in one liter of water. The following concentrations were subsequently made from the stock solution: 0.005, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 wt. percent. Surface tension measurements were made using a Fisher Brand Model #20 Surface Tensiometer.

Each solution was placed in the clean glass vessel and placed on a sample table. The sample table was manipulated until it was directly beneath a platinum-iridium ring, raised to immerse the ring until it was in the test liquid at 1/8 inch, then lowered until breaking of the distended film occurred. The scale reading at the "liquid-surface breaking point" was recorded as the apparent surface tension.

3.10.2 Determination of the Solubility of PCBs in Witconol Solutions

Several 125 mL Erlenmeyer flasks were spiked with 500 μL of 100 mg/L AR 1254 solution. The contents were blown down with a small stream of nitrogen. Twenty-five milliliters of the surfactant solutions were placed in their appropriate flasks and the latter shaken for 24 hr. The solutions were transferred to 40 mL vials and extracted twice with 5 mL of hexane.

Witconol SN-70 was prepared at multiple concentrations of its CMC (2x, 4x, and 8x CMC). Three 125 mL Erlenmeyer flasks were spiked with 10,000 mg/L AR 1254 and one flask was spiked with 6,500 ppm AR 1254. The contents in each flask were blown down with a small stream of nitrogen under a fume hood until the viscous aroclor located on the bottom was visible. A 25 mL aliquot of Witconol SN-70 solution was added to each flask and the latter were agitated for 24 h. The supernatant was carefully siphoned to allow small globules of undissolved PCBs to remain in the flasks. The surfactant solutions were extracted twice with 5 mL of hexane. A 1:50 dilution was performed on the hexane extract; 1 mL was placed in an autosampler vial, and 5 µL of internal standard were added. The flasks containing undissolved PCBs were dried overnight and extracted twice with 5 mL of hexane. A 1:100 dilution was performed on the hexane extracts, and 1 mL of each extract placed in an autosampler vial along with 5 µL of internal standard. The samples were analyzed by GC/ECD using conditions outlined in Section 3.5.

3.11 Investigating PCB Extraction from Soil Using Witconol SN-70

3.11.1 Desorption of PCBs from Soil by Witconol SN-70 as a Function of Time and Temperature

A 0.5 wt % solution of Witconol SN-70 was prepared by placing 25 mL of 2% Witconol SN-70 in 100 mL of 18 MΩ water. Five grams of soil was placed in each of ten 125 mL Erlenmeyer flasks and 25 mL of surfactant solution was added. One flask was immediately centrifuged and decanted into a 40 mL amber vial. The remaining nine flasks were agitated at room temperature for the following times: 0.1, 0.5, 1, 2, 4, 8, 12, 20, and 24 h. The flasks were centrifuged at 2500 rpm for 20 min, the supernatant decanted, the samples extracted with 2 x 5 mL of hexane, internal standard added, and the extract analyzed per in Section 3.6. The experiment was repeated at 30°C and 40°C in an oven, with agitation done by using a Fisher Specimen Tube Rotator, while all other conditions remained the same.

3.11.2 Investigating the Effect of Electrolyte on PCB Desorption from Soil

Several inorganic electrolytes were chosen for this experiment: Ca $(NO_3)_2$, KNO_3, $Sr(NO_3)_2$, $NaNO_3$, $NaSO_4$, and NaCl. Each salt was prepared at 0.3M concentration in 0.1 wt % Witconol SN-70 solution. Five grams of AR 1254 laden soil was placed in each of several 125 mL Erlenmeyer flasks and 25 mL of the electrolyte-containing surfactant solutions added. The flasks were agitated mechanically for 24 h, transferred to a 40 mL volumetric vial and centrifuged for 10 min. The supernatant was extracted and analyzed as per Section 3.5.

3.11.3 Investigating The Effect of pH on the Desorption of PCB from Soil

Experiments were conducted to investigate the effects of pH on the surfactant enhanced desorption of PCBs from soils. Witconol SN-70 was prepared at a 0.10 wt % and its pH measured using a Accumet Model 150 pH meter. Twenty five mL of solution was placed in each of four 125 mL Erlenmeyer flasks along with five grams of soil. The flasks were swirled briskly to homogenize the contents. The pH of the soil and surfactant solutions was measured, then adjusted using 1:1 HNO_3 or 0.5 M NaOH solution. The flasks were capped and shaken mechanically for 24 h and the solutions centrifuged for 20 min @ 2500 rpm. The pH of the surfactant solutions were measured after equilibration. The supernatants were collected in 40 mL vials and extracted twice with 5 mL of hexane, five μL of PCNB was added to 1 mL of each extract, and then analyzed by GC/ECD per Section 3.6. The experiment was repeated using 0.25 wt % surfactant solution.

3.11.4 Effect of Organic Additives on PCB Solubilization

The organic additives used were ethanol, methanol, 2-propanol, and butanol at 0.3M in 0.1 wt % Witconol SN-70 and in 0.25 wt % Witconol SN-70. The appropriate volumes were placed in 100 mL of the surfactant solution. Five grams of soil was placed in a series of 125 mL Erlenmeyer flasks. Twenty-five mL of the surfactant solution containing a different organic additive was placed in its respective flask. The flasks were agitated and the supernatants were extracted and analyzed as per Section 3.5.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Physicochemical Characteristics of Soil

Particle size analysis of the soil indicates that the soil is of a sandy nature. This can be observed from the particle size distribution curve shown in Figure 4.1. The soil was not retained on the #4 sieve, therefore indicating the absence of gravel. Two percent of the sample passed through the #200 clay fraction sieve. The soil is therefore a 98/2 sand/clay matrix. The high sand content can facilitate the desorption of PCBs from the soil, as it is generally known that organics are less strongly bound to a sandy matrix in comparison to one of high clay content.

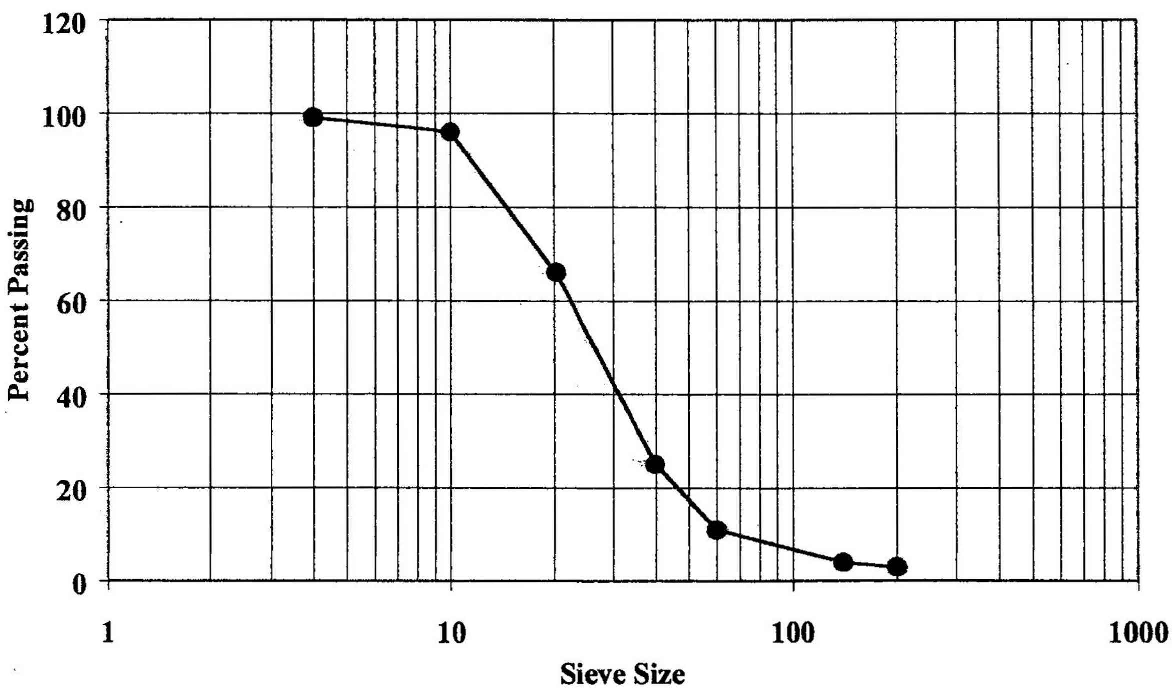


Figure 4.1: Particle Size Distribution Curve of Soil

Other physicochemical characteristics presented in Table 4.1 indicate that the soil was very dry, contained low cation exchange capacity and low organic content. As the particle size decreased, AR 1254 concentration increased (Figure 4.2).

Table 4.1: Soil Quality Parameters

Soil Quality Parameter	Results
Sieve Analysis	Sandy Soil (98/2 Sand/Clay)
Total Organic Carbon	0.93%
Cation Ion Exchange	1.7×10^{-4} mol Na/g
pH	5.1
Surface Area Analysis	7.5 m^2/g
Percent Dry Weight	99.7

Surface area analysis indicates that the surface area was inversely proportional to particle size. The smaller the particles the higher the surface area (Figure 4.3)

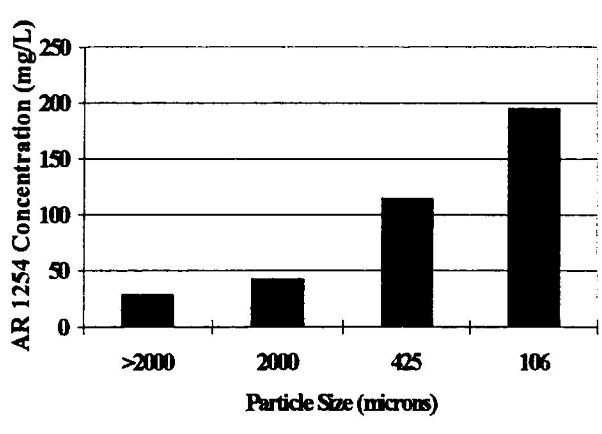


Figure 4.2: Relative Distribution of PCB Versus Particle Size

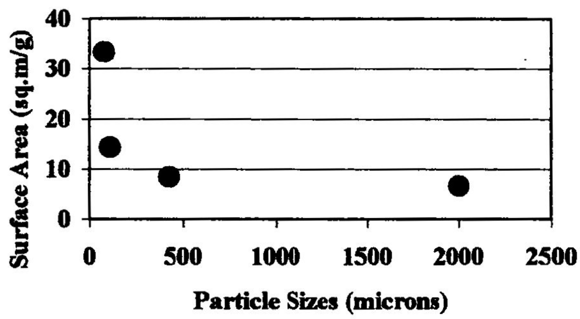


Figure 4.3: Soil Particle Size Distribution Versus Surface Area

4.2 Concentration and Distribution of PCB in Soil

The soil was spiked to contain 100 mg/kg as the basis for the extraction experiments. The average concentration determined by Soxhlet extraction of the soil and analysis by GC-ECD was 104 mg/kg of PCB AR 1254 (Table 4.2).

Table 4.2: Concentration of PCB in Spiked Soil

Sample Number	PCB Concentration (mg/kg)
Sample 1	101
Sample 2	107
Average	104

The distribution of PCBs as a function of particle size and the results are shown in Figure 4.2. Higher loadings were found on smaller particles. This is consistent with the increasing surface area and increase in the number of possible absorption sites as the soil particle sizes become smaller.

increasing surface area and increase in the number of possible absorption sites as the soil particle sizes become smaller.

4.3 Surfactant Screening for the Removal of PCB AR 1254 from Soil

The PCB removal data (Tables 4.3 and 4.5) is an approximation, since significant matrix interference was experienced during extraction and analysis which prevented accurate PCBs quantitation. However, a qualitative assessment of the chromatograms was undertaken to compare the relative performance of the surfactants. In each chromatogram from the surfactant extracts, comparisons were made by taking the ratio of the heights of five AR 1254 peaks to that of the internal standard (IS). The larger the area of AR 1254 peaks compared to that of the internal standard, the greater the amount of PCBs present in the extract. Performance was rated as follows:

High = Greater than 85% PCB removed

Medium = Greater than 50% PCB removed

Low = Less than 50% PCB removed

Surfactants prepared at their CMCs or at very low wt./volume % were not effective in desorbing the PCBs from the soil (Table 4.3 and 4.4). However, at concentration 10x CMC or wt./volume %, SDS, 1-DPC, and Witconol SN 70 were highly effective in dissolving PCBs; Igepal CA 720, Witcodet 100 and Triton X-100 were ranked as medium in their performance, and DDAB, Brij 30, Alcodet and Witcolate D51-51 were ineffective. The extracting activities of the surfactants were referenced to that of pure water which showed no activity in removing PCBs from soil. The approach to deciding the amount and concentration of each surfactant used in the extraction process was based on the micellar phenomena. It is known that at certain concentration, the critical micelle concentration, surfactants form micelles in water and other solvents. These surface active agents are most effective in extracting contaminants (such as polyaromatic hydrocarbons) from soil surfaces at concentrations equal to or greater than their CMC.

Table 4.3: The Effect of Surfactants at their CMC on the Removal of PCBs from Spiked Soil

Surfactant	Formula/Class	CMC (M)	Molarity used in study	% Surfactant in extraction media	Approximate AR1254 Concentration Remaining in soil after washing (mg/Kg)
SDS	$CH_3(CH_2)_{11}OSO_3Na$	$1.2x10^{-2}$	$1.2x10^{-2}$	0.35 wt %	94
1-DPC	$C_{12}H_{25}Pyr^+Cl^-$	$1.7x10^{-2}$	$1.7x10^{-2}$	0.48 wt %	87
Igepal CA 720	$4\text{-}(C_8H_{17})C_6H_4O(CH_2CH_2O)_{11}CH_2CH_2OH$	$3.7x10^{-4}$	$3.7x10^{-4}$	0.03 wt %	100
Triton X 100	*p-t* $C_8H_{17}C_6H_4O(C_2H_4O)_{10}H$	$3.3x10^{-4}$	$3.3x10^{-4}$	0.02 wt %	100
Witcodet 100	Alkylbenzene Sulfonate/ Alcohol Ethoxylate	UNK	UNK	0.05 vol %	100
Alcodet HSC 1000	Thioethoxylate	UNK	UNK	0.05 vol %	100
Witcolate D51-51	Alkyl Phenoxyether Sulfate	UNK	UNK	0.05 vol %	100
DDAB	$CH_3(CH_2)_{11}N(C_2H_5)(CH_3)_2Br$	$1.6x10^{-2}$	$1.6x10^{-2}$	0.03 wt %	100
Brij 30	$C_{12}H_{25}(OCH_2CH_2)_4OH$	$6.4x10^{-5}$	$6.4x10^{-5}$	0.002 wt %	100
Deionized Water	N/A	N/A	N/A	N/A	100

UNK = Unknown, 0.05 wt/v% used instead of CMC
N/A= Not Applicable

Table 4.4: The Effect of Surfactants at Tenfold their CMCs on the Removal PCBs from Spiked Soil

Surfactant	Formula/Class	CMC (M)	Molarity used in study	%Surfactant in extraction media	Approximate AR1254 Concentration in soil after washing (mg/Kg)
SDS	$CH_3(CH_2)_{11}OSO_3Na$	$1.2x10^{-2}$	$1.2x10^{1}$	3 wt. %	6
1-DPC	$C_{12}H_{25}Pyr^+Cl^-$	$1.7x10^{-2}$	$1.7x10^{-1}$	4.8 wt. %	4
Igepal CA 720	4-$(C_8H_{17})C_6H_4O(CH_2CH_2O)_{11}CH_2OH$	$3.7x10^{-4}$	$3.7x10^{-3}$	0.3 wt. %	4
Triton X 100	p-t $C_8H_{17}C_6H_4O(C_2H_4O)_{10}H$	$3.3x10^{-4}$	$3.3x10^{-3}$	0.2 wt. %	4-9
Witcodet 100	Alkylbenzene Sulfonate/ Alcohol Ethoxylate	TBD	TBD	0.5 vol. %	35
Alcodet HSC 1000	Thioethoxylate	TBD	TBD	0.5 vol.. %	75
Witcolate D51-51	Alkyl Phenoxyether Sulfate	TBD	TBD	0.5 vol.%	93
DDAB	$CH_3(CH_2)_{11}N(C_2H_5)(CH_3)_2Br$	$1.6x10^{-2}$	$1.6x10^{-1}$	0.3 wt.%	99
Brij 30	$C_{12}H_{25}(OCH_2CH_2)_4OH$	$6.4x10^{-5}$	$6.4x10^{-4}$	0.02 wt. %	100
Deionized Water	N/A	N/A	N/A	N/A	100

UNK=0.5 wt./v% used instead of CMC
N/A=Not Applicable

Table 4.5: Qualitative Assessment of PCBs in Surfactant Extract Versus PCBs Residue in Soil Using Surfactant at CMC at low Vol. %

Surfactants	Ratio of AR 1254 to IS Peak from Surfactant Extracts	Ratio of AR 1254 to IS in Hexanes extracts of Soils After Surfactant Treatment
SDS	High	Low
DPC	High	Low
Witconol SN 70	High	ND
Igepal CA720	Medium	Medium
Witcodet100	Medium	Medium
Triton X 100	Medium	Medium
DDAB	Very Low	High
Brij-30	Very Low	High
Alcodet HSC1000	Very Low	High
Witcolate D51-D51	Very Low	High
Pure Water	Very Low	High

ND= Not Determined
IS = Internal Standard

4.4 Matrix Interferences in PCB Extraction and Analysis

The analysis of PCB concentrations in both the surfactant extracts and in the soils remaining after extraction requires that the PCBs be first extracted into hexane. However, this process was significantly affected by matrix interferences, most likely from the various surfactants. The extraction of PCBs from each surfactant into hexane by liquid-liquid extraction resulted in the formation of an emulsion from which it was difficult to retrieve the volume of hexane added. The amount of hexane recovered varied from 60% to 95%. Similarly, during the hexane extraction of PCB from the soil, a persistent emulsion formed during the required sulfuric acid cleanup step. It was therefore imperative that the matrix problem be addressed in order to improve the accuracy of the PCB quantitative analysis.

Several approaches were explored to break or prevent the emulsion, including the following: (1) the addition of electrolytes sodium, calcium, and aluminum salts; (2) filtering the emulsion through glass wool; (3) mechanical vortexing; (4) the addition of alcohols; (5) using mild liquid-liquid extraction; and (6) solid phase extraction (SPE). Mild liquid-liquid extraction averted the formation of the emulsion, but the kinetics of extraction required over 24 hr. for completion. Solid phase extraction showed reasonable potential but the extraction process was tedious, with the cartridges frequently showing very slow and uncontrollable filtering rates and, hence, unpredictable and inconsistent levels of recoveries. The SPE cartridges were unable to cope with the relatively viscous surfactant solutions.

The use of alcohols to break the emulsion gave the most successful results. In SDS surfactant solutions prepared at both the CMC and 10x CMC, PCBs were spiked at 10 mg/L and 100 mg/L. The samples were agitated to form emulsions. A few drops of isopropyl alcohol were added to the emulsions and separation of the organic and aqueous layer occurred within five minutes. Greater than 98% recovery of the hexane extracts was attained. Although the added volume of hexane was successfully recovered, another challenge was that the PCBs spiked in the surfactant gave less than 100% recovery into hexane and the percent recovery varied with the surfactant concentration. A more extensive investigation was, therefore, performed to determine the recovery of PCBs from a wider range of surfactants and as a function of concentrations of the latter. The idea is to achieve constant recovery of PCBs from the surfactant solutions independent of the concentration of the surfactant within the range investigated. This will enable a more accurate quantitation of the PCBs.

4.5 Recovery of PCBs from Surfactant Solutions

Figure 4.4 shows the recovery of 50 mg/L PCB AR 1254 from Brij 30 surfactant solution at the 1x, 5x, and 10x CMC in hexane, (corresponding to 0.023, 0.115, and 0.23 mmol/L, respectively). At the CMC, 39% of the AR 1254 was recovered. At 5x CMC, 53% of AR 1254 was recovered, and at 10x the CMC, 71% of the AR 1254 was recovered from Brij 30. The graph shows that the PCB recovery is linearly dependent on the surfactant concentration over the concentration range investigated. A very consistent recovery trend was observed. A constant recovery over the range of surfactant concentration studied is desirable but was not observed.

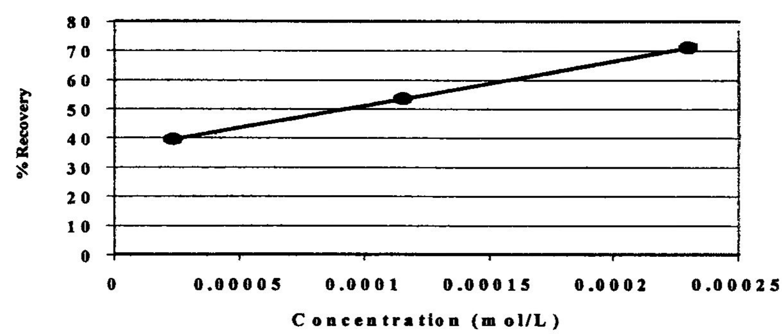


Figure 4.4: Recovery of AR 1254 from Various Concentrations of Brij 30
(1 x CMC=2.3 x 10^{-5} mol/L, 5 x CMC=1.15 10^{-4} mol/L, 10 x CMC=2.3 x 10^{-4} mol/L)

The recovery of AR 1254 from Witcolate D51-51 is shown in Figure 4.5. The amount of AR 1254 recovered increases as the surfactant concentration increased. PCBs recovery into hexane was less than 60% of the spiked 50 mg/L in the most concentrated surfactant solution to as low as 10% in the lowest surfactant concentration. Although a consistent trend was observed, the recovery was not constant over the range of surfactant concentration studied.

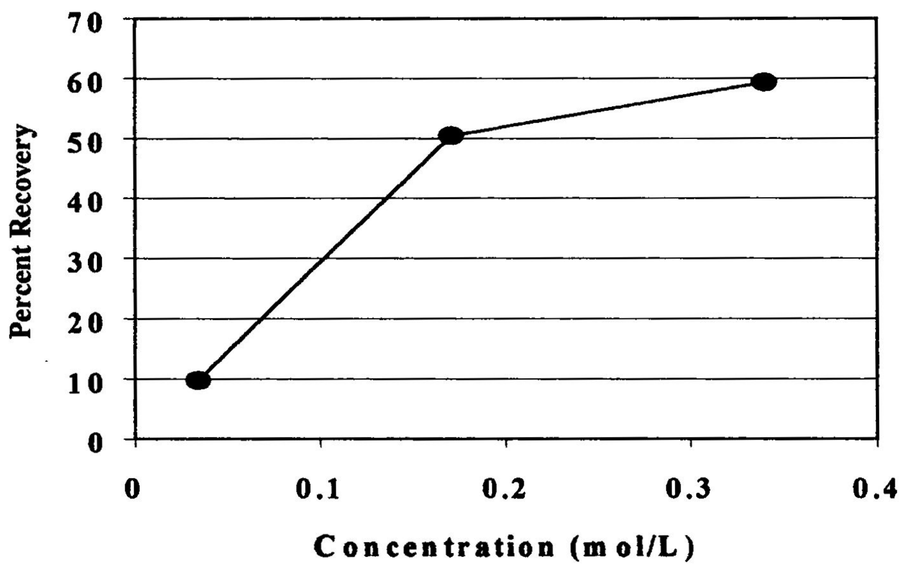


Figure 4.5: Recovery of AR 1254 from Various Concentrations of Witcolate D51-51
(1 x CMC=0.034mol/L, 5 x CMC=0.17 mol/L, 10 x CMC=0.34 mol/L)

The amount of AR 1254 recovered from Witcodet 100 decreased as the surfactant concentration increased (Figure 4.6). This response is in direct contrast to the previous cases of Witcolate D51-51 and Brij 30, and suggests that the PCBs have an increased affinity for this surfactant with increase in surfactant concentration. This is consistent with the general knowledge that as the concentration of the surfactant increases, so does its ability to solubilize a hydrophobic contaminant. At 0.25 wt %, 44 ppm of the PCBs was recovered and at 5 wt %, 31 ppm was recovered. As previously stated, it is desirable to have high and consistent recovery of the PCBs over a range of surfactant concentration.

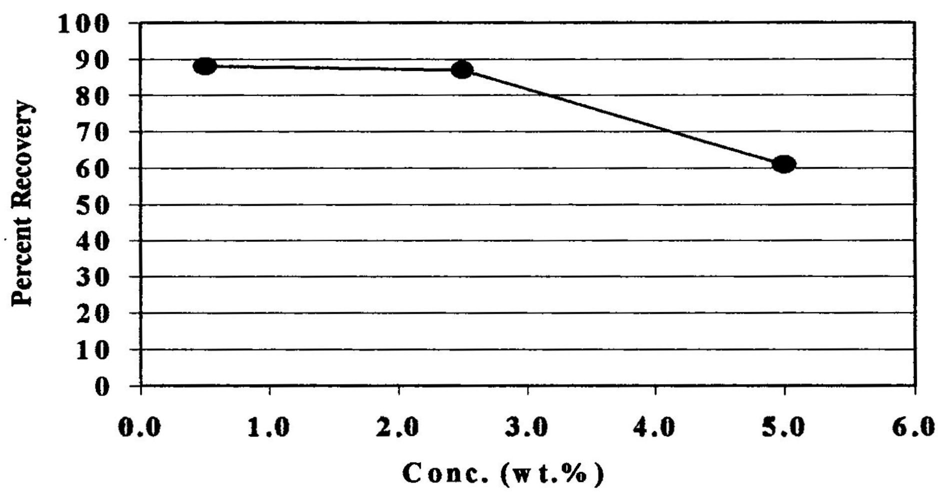


Figure 4.6: Recovery of Aroclor 1254 from Various Concentrations of Witcodet-100

PCBs recovery from Witconol SN-70 is shown in Figure 4.7. At 0.5x CMC (0.25 wt %) it was 88% (44 ppm of 50 ppm). For the remaining concentrations, 1x, 2x, 5x and 10x CMC, the recoveries of Witconol SN-70 were 97%, 97% and 93%, respectively. As the concentration of Witconol SN-70 varied, the amount of AR 1254 recovered remained high and relatively constant.

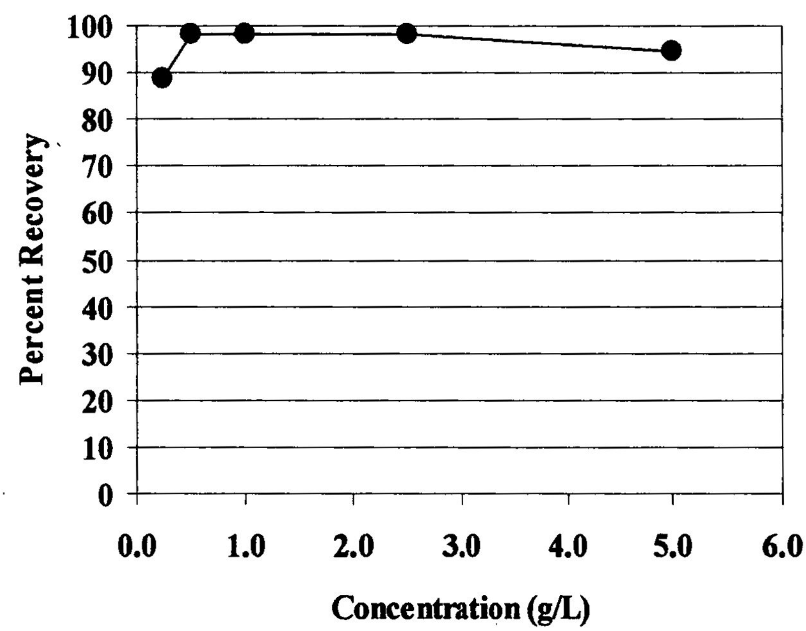


Figure 4.7: Recovery of AR 1254 from Various Concentrations of Witconol SN-70
(1x CMC=0.05 wt.% , 2x CMC=0.1 wt.%, 5x CMC=0.25 wt.%, 10x CMC=0.5wt.%)

The recovery of PCBs from Triton X-100 was investigated at various concentrations (Figure 4.8). As the concentration of the surfactant increased, the amount of PCB recovered from the solution also increased. The recovery goes from 55% to 83% from the 1x CMC to 5x CMC, respectfully. At 10x CMC, the recovery into hexane was 86% (43 ppm of 50 ppm). Here again, the recoveries vary significantly with surfactant concentration.

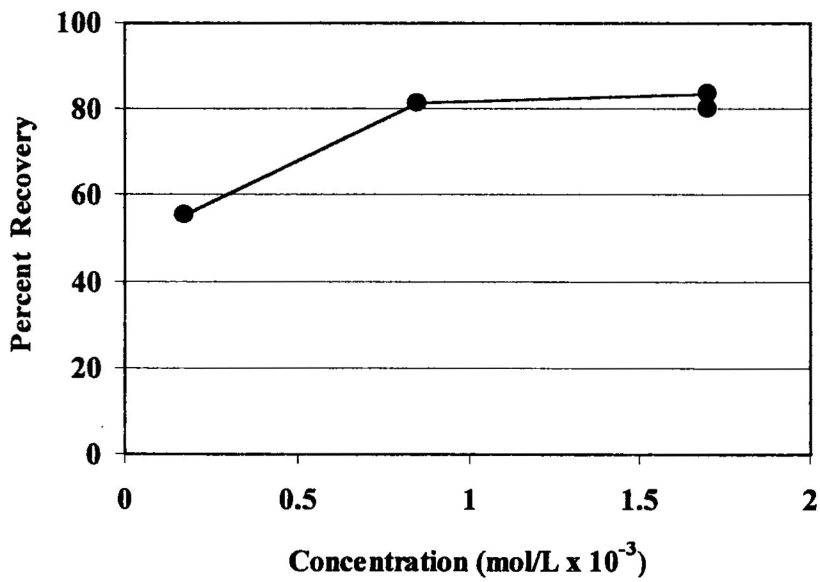


Figure 4.8: Recovery of AR 1254 from Various Concentrations of Triton X- 100
(1x CMC=0.00017mol/L, 5x CMC=0.00085 mol/L, 10x CMC=0.0017 mol/L)

Like Witcodet 100, the recovery of AR 1254 from SDS shows a reverse trend (Figure 4.9). As the concentration of the surfactant increases, the amount of AR 1254 recovered decreases. The recovery goes from 79% at 1x CMC to 61% at 5x and remained essentially constant as the concentration of the surfactant increased to 10x CMC. SDS shows variation in PCB recovery over the range of surfactant concentrations studied.

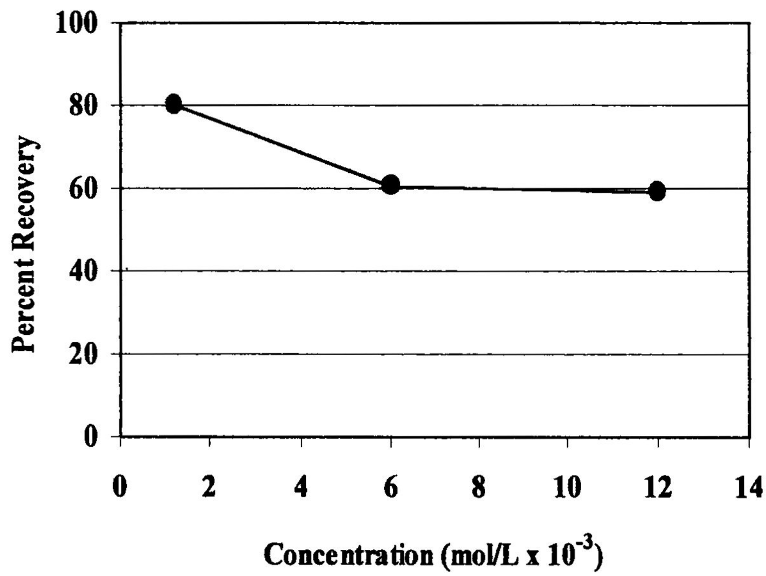


Figure 4.9: Recovery of AR 1254 from Various Concentrations of SDS
(1x CMC=0.0012 mol/L, 5x CMC=0.006 mol/L, 10x CMC=0.12 mol/L)

Witconol SN-70 shows fairly constant and high recoveries over a range of surfactant concentrations in comparison to the others investigated. PCB recoveries in hexane ranged from 88% from the surfactant solution at the CMC to as high as 97% at

10x CMC. This surfactant was also reported to be a promising candidate for PCB removal from soil.[4] Based on its extraction enhancing potential and the its ability to allow high and consistent recovery of PCBs from its matrix, this surfactant was chosen for further soil extraction studies.

Prior to its use in extraction, its CMC was verified in order to more confidently choose the appropriate concentration range for most efficient extraction studies. The solubility of AR 1254 in Witconol SN-70 as a function of the surfactant concentration was also determined in order to ascertain the extraction capacity of the surfactant in reference to its extraction capabilities. Figure 4.10 shows a plot of surface tension versus the log surfactant concentration.

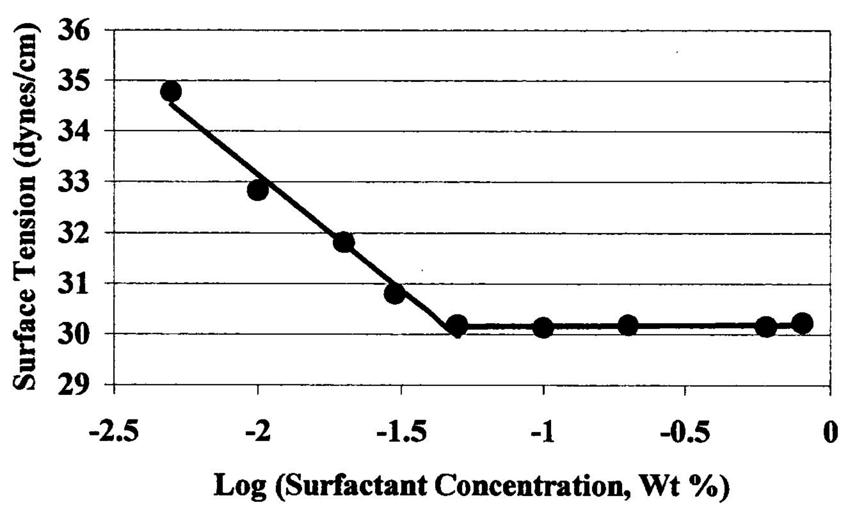


Figure 4.10: Plot of Surface Tension Versus Log (surfactant concentration)

A sharp change in the surface tension was observed at -1.30103 (log surfactant concentration) corresponding to the surfactant CMC of 0.05 wt %.

4.6 PCB Solubility as a Function of Witconol SN-70 Concentration

The solubility of AR 1254 in Witconol SN-70 as a function of surfactant concentration is shown in Figure 4.11. Below the surfactant CMC, AR 1254 solubility was extremely low. At and above the CMC, the solubility of AR 1254 increased linearly with surfactant concentration. This is consistent with the micellar concept discussed in Chapter 2. At the CMC, surfactant micelles create the hydrophobic cavities within the aqueous phase into which PCBs can be dissolved. The higher the surfactant concentration, the greater the number of micelles formed, and the greater its extraction capacity.

4.7 PCB Extraction from Soil Using Witconol SN-70

The amounts of PCBs removed from the soil is far below the surfactant's dissolving capacity. For example, from Figure 4.11, a 0.5 wt % (5 g/L) surfactant solution (10xCMC) is capable of dissolving approximately 3500 to 4000 mg/L of PCBs.

Figure 4.12 shows the removal of PCBs from the soil as a function of surfactant concentration. The figure shows that using surfactant solution at concentration 10x its CMC, 50% of the PCBs was removed, and at 100x the CMC, 100% removal of the PCBs was achieved.

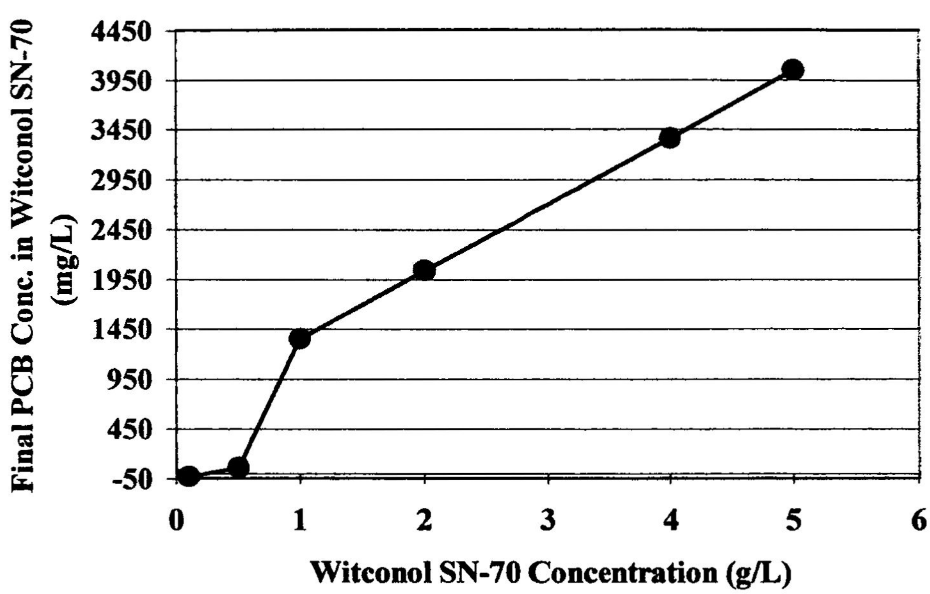


Figure 4.11: PCB Solubility Versus Witconol SN-70 Concentration

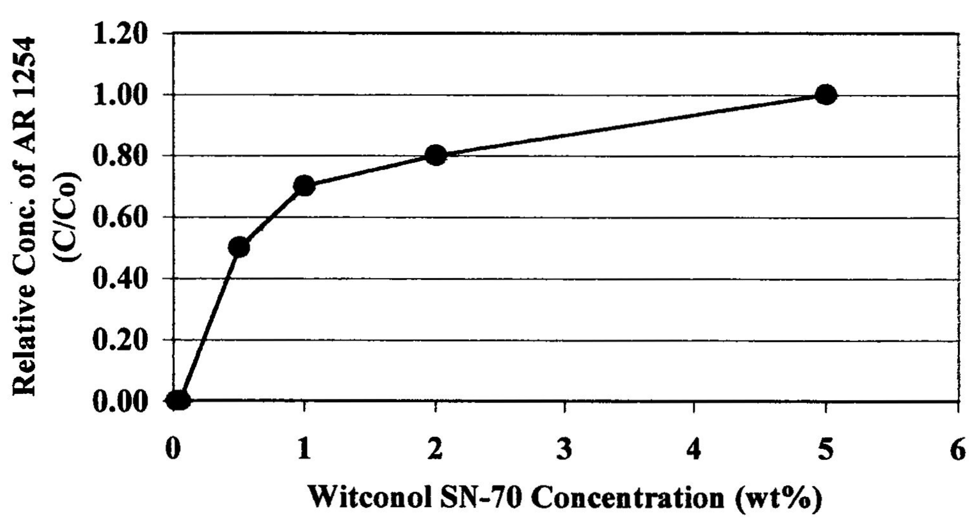


Figure 4.12: Removal of PCBs from Soil as a Function of Surfactant Concentration
(Temp. 25°C, Time 24 h, Initial conc. of PCBs in soil, 100 mg/kg)

However, the surfactant solution at this same concentration removed only 50% (25 ppm) of the possible 50 ppm that was removable. The surfactant effectiveness can be hampered because of mass transfer limitations. A 100% removal was only achieved with 5 wt % (100x CMC) surfactant solution. Figure 4.13 shows that at 25 ^{0}C PCB

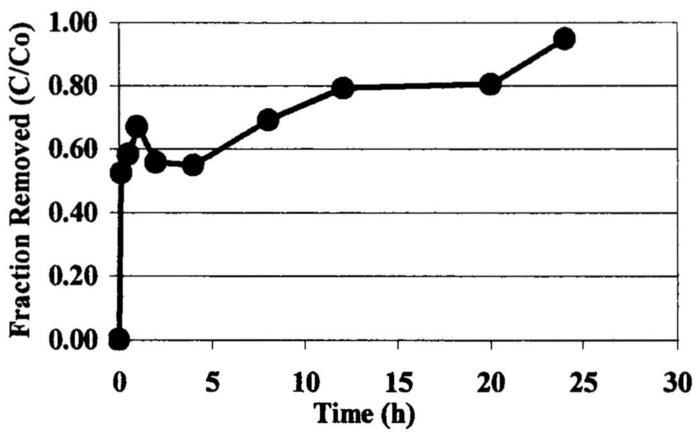


Figure 4.13: PCB Removal vs. Time at 25^{0}C Using 5 Wt% Witconol SN-70
(Temp. 25^{0}, Maximum removable conc. of PCBs, 50mg/L)

removal peaked at approximately 70% within the first two hours of extraction. Subsequently, the amount of PCBs removed was reduced and then gradually increased to 100% at 24 h. The initial peaking of kinetics could be due to the behavior of the surfactant in solution under agitation conditions. Surfactant micelles present at the beginning of extraction were very effective in dissolving PCBs from the soil.

4.8 The Effect of Temperature on the Surfactant Desolubilization of PCBs from Soil

Figures 4.14 and 4.15 show PCB removal from soil with time at various temperatures, using 5 wt % Witconol SN-70.

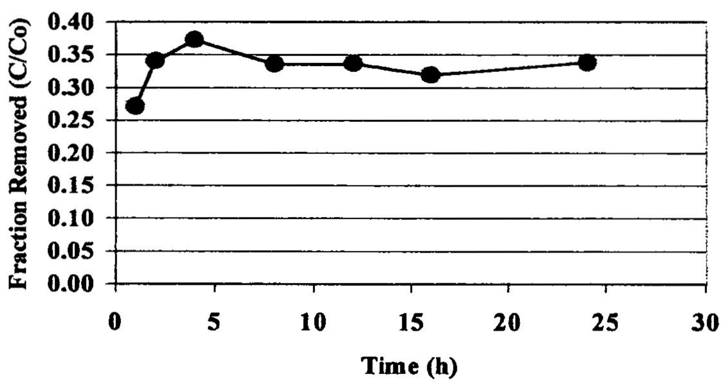


Figure 4.14: PCB Removal vs.Time at 30 °C Using 5 Wt % Witconol SN-70
(Maximum removable conc. of PCBs, 50mg/L)

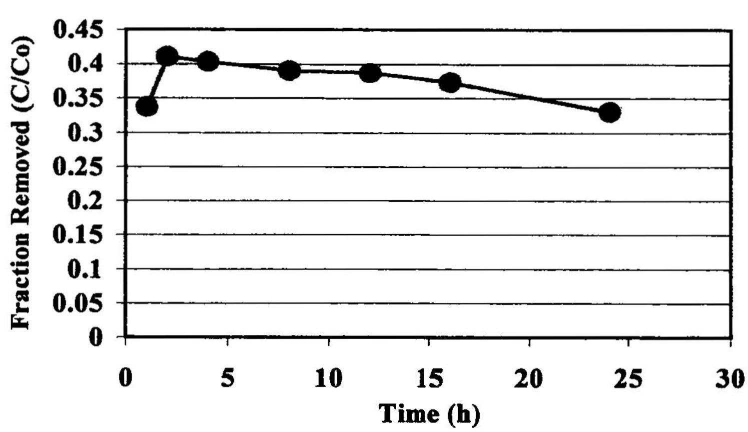


Figure 4.15: PCB Removal vs. Time at 40 °C Using 5 Wt % Witconol SN-70

Continuous agitation could disturb the micellar structure, thereby causing them to be less effective. As time progressed, the micelles could be reorganized and increase the amount of PCBs removed.

As the temperature was increased to 30 °C, it was observed that rate of removal was slower than at 25 °C, and the final amount of PCBs removed was less. The amount of PCBs dissolved was maximum around 38%, within 4 h, thereafter remaining constant for the duration of the run. A similar trend was observed for soil extraction done at 40 °C. The amount of PCBs dissolved was maximum around 40%, within 2 h. In this case, however, there was a slight continuous decrease in the amount of PCBs dissolved beyond 2 h through 24 h. The reduction in PCB extraction efficiencies as the temperature was increased from ambient to 30 and 40 °C could be due to changes in the micelles. As the temperature is increased, the surfactant monomers have increased kinetic energy and are highly mobile in solution. This mobility decreased their tendency to aggregate to form micelles, thereby reducing their extraction power. According to Rosen, although temperature increase causes decreased hydration of the hydrophilic group, which favors micellization, temperature increase also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization.[12] A decrease in the CMC was possible, and would mean less extraction of the hydrophobic contaminant.

4.9 The Effect of pH on Surfactant Removal of PCBs from Soil

Figure 4.16 shows the change in the amount of PCBs dissolved versus the adjusted pH of the soil-surfactant slurry using 0.1 wt % (2x CMC) surfactant solution.

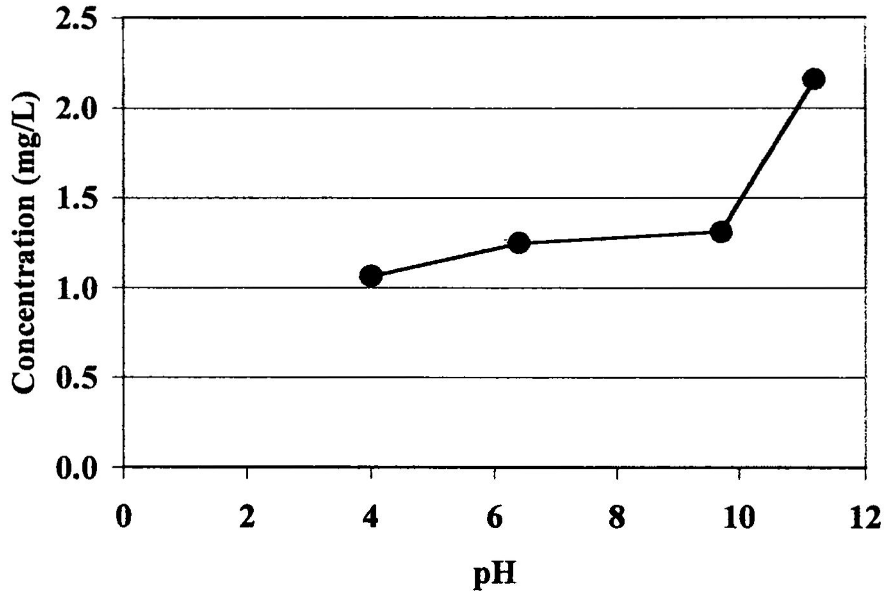


Figure 4.16: The Effect of pH on the Removal of PCBs from Soil Using 0.1 Wt % Witconol SN-70 (25 °C, 24h)

The figure shows that at this surfactant concentration, the amount of PCBs removed was between 1 and 2.5 mg/L corresponding to 2% and 5%, respectively, although small increases in the removal efficiencies were observed as the pH was adjusted from 4.1 to 10. This is most likely due to the high buffering capacity of the soil which imposed significant resistance to change in pH and kept the equilibrium pH in the range of 4.4 to 6.0 (Table 4.6).

Figure 4.17 shows the variation in the amount of PCBs extracted versus the adjusted pH of the soil-surfactant slurry at a higher concentration of 0.25 wt % (5x CMC) surfactant solution.

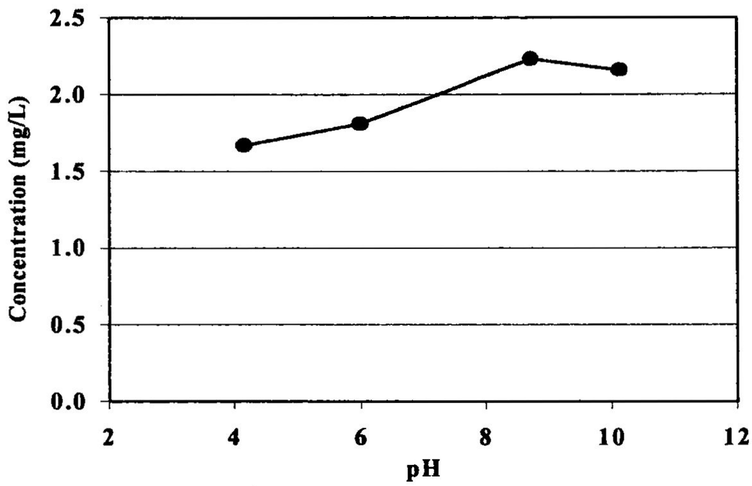


Figure 4.17: The Effect of pH on the Removal of PCBs from Soils with Witconol SN-70 at 5x the CMC

Table 4.6: Initial, Adjusted, and Equilibrium pH

Flask	Surfactant Concentration (wt %)					
	0.10			0.25		
0	Initial pH	Adjusted pH	Final pH	Initial pH	Adjusted pH	Final pH
1	5.1	4.0	4.4	5.0	4.1	4.6
2	4.6	6.4	5.3	4.6	6.0	5.4
3	5.0	9.7	5.5	5.1	8.7	5.7
4	5.1	11.2	5.9	5.1	10.1	6.0

The figure shows that at this surfactant concentration, the actual amount of PCBs removed was 10% of the total available. However, small increases in the removal efficiencies were observed as the pH was increased from 4.14 to 10.0. It was also noted that the equilibrium pH was much less than the adjusted pH and was close to the natural pH of the soil (Table 4.6). The adjusted initial pH was therefore not sufficient to overcome the buffering capacity of the soil. In general, changes in the pH of the soil surfactant slurry resulted in no significant increase in the extraction of the PCBs from the soil using this nonionic surfactant.

4.10 The Effect of Electrolytes on Surfactant Removal of PCBs from Soil

Figure 4.18 displays the percent removal of AR 1254 from soil in the presence of 0.3 M concentrations of various electrolytes added to the surfactant solutions. The figure show that in the presence of inorganic monovalent and divalent cations and anions, the extraction efficiency of the surfactant was significantly reduced. For electrolytes in a 0.1 wt % surfactant solution, the maximum fraction of PCBs removed was approximately 0.13 or 13% of the amount removeable with K and decreased to 6.9% with Sr. The order in which the cations affected (reduced) extraction efficiency was as follows: $K^{+} < Na^{+} < Ca^{2+} < Sr^{2+}$. For the anions, the order was $Cl^{-} < NO_3^{-} < SO_4^{2-}$. Experiments with NaCl were performed in duplicate. This result suggests that periodicity affects the extraction efficiency of the surfactant. The presence of electrolytes in surfactant solutions can bring about a change in the CMC. The change in the CMC of nonionics and other surfactants by the addition of electrolyte has been attributed [20,21] to the "salting in" and salting out of the hydrophobic groups in the aqueous solvent by the electrolyte, rather than to the effect of the latter on the hydrophilic groups of the surfactant. The energy required to accommodate a nonpolar solute is changed in electrolyte solution because of water-ion interactions.[22] This results in a change in the activity coefficients of the solute. If the required energy is increased by the presence of the electrolyte, then the activity coefficient of the solute is raised and the solute is "salted out." If the energy required is decreased, then the solute is "salted in." When the monomeric form of the surfactant is salted out by the presence of an electrolyte, micellization is favored and the CMC of the surfactant is decreased. When the monomeric form is salted in by the electrolytes, the CMC is increased. The total effect of an electrolyte appears to approximate the sum of its effects on various parts of the solute in contact with aqueous phase. Since the hydrophilic groups of the surfactant molecules are in contact with the aqueous phase in both monomeric and the micellar form of the surfactant, and the hydrophobic groups are in contact with the aqueous phase only in the monomeric form, the effect of the electrolyte on the hydrophilic groups in the monomeric and in the micellar forms may be the same, leaving the hydrophobic groups in the monomers as the moiety most likely to be affected by the addition of an electrolyte to the aqueous phase.[16]

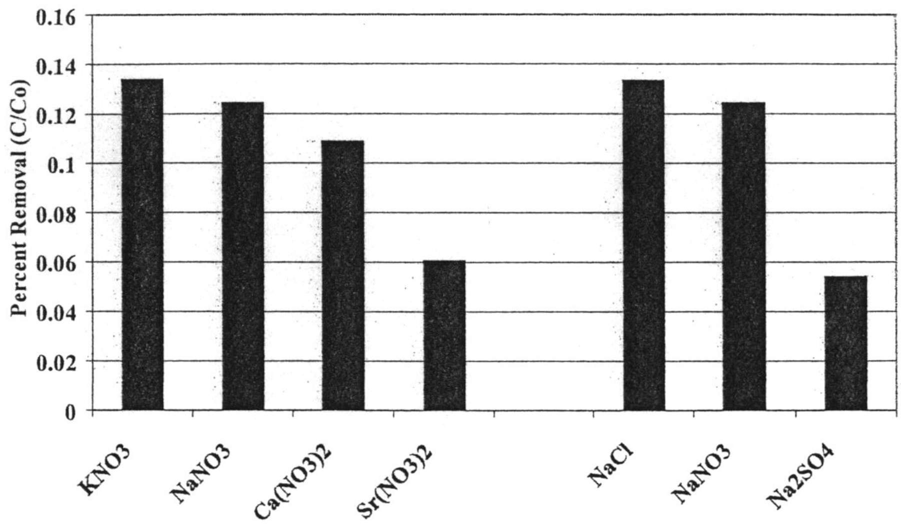


Figure 4.18: PCB Removal Using 0.3 M Electrolytes in 0.1 Wt % Witconol SN-70

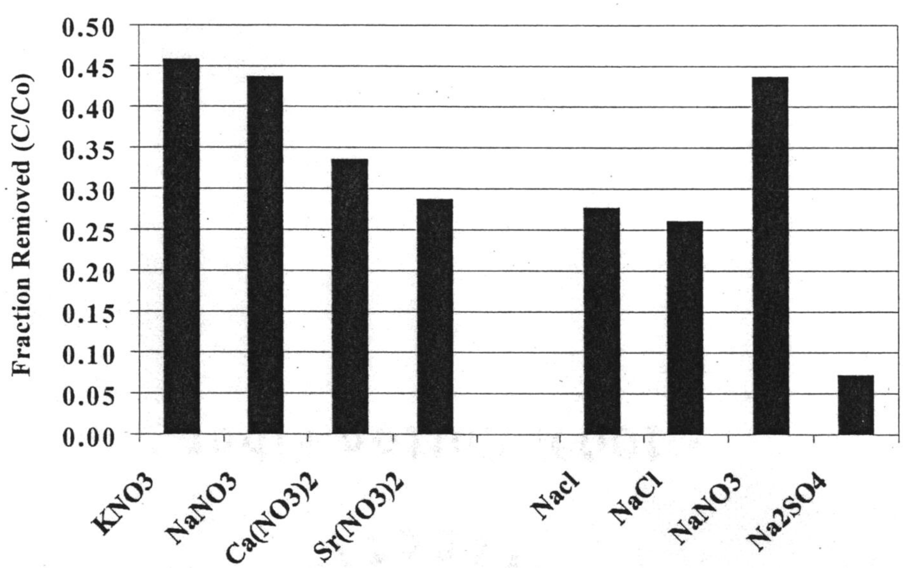


Figure 4.19: PCB Removal Using 0.3 M Electrolytes in 0.25 Wt % Witconol SN-70

Using a more concentrated surfactant solution of 0.25 wt % (5x the CMC), an overall similar behavior was observed in which the presence of the electrolytes resulted in a reduction in the extraction efficiency of the surfactant (Figure 4.19). There again the order in which the cations affected (reduced) solubilization was as follows: K^+<Na^+<Ca^{2+}<Sr^{2+}. For the anions, the order was NO_3^-<Cl^-<SO_4^{2-}.

Table 4.7: Hydrated Ionic Radii

Ions	Hydrated Radii (Angstrom)
K	3.31
Na	3.58
Ca	4.2
Sr	NK

NK= Not Known

Whereas trends in the effects of the anions are not readily explained, the effects of the cations may be related to their ionic radii; the greater the radius of the hydrated ions, the greater their effects on decreasing the surfactant efficiency.[23,24] Table 4.7 lists the ions utilized and their hydrated radii. As the hydrated radii increase, the effects of the electrolytes also increase.[25] One possible reason stems from the decrease in mutual repulsion of the ionic head groups in the presence of the electolytes which causes close packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume available for solubilization of compounds.[12]

4.11 The Effect of Low Molecular Weight Alcohol Additives on PCB Solubilization

Upon addition of organic additives, the energy required for micellization is decreased. Straight chain molecules have a tendency to reduce the CMC, as opposed to branched molecules, but at the same time, the length of the hydrophobic group increases. The rationale is that molecules that are most effective at reducing the CMC are dissolved in the outer portion of the micelle and are under lateral pressure, tending to force them into the inner portion of the core of the micelle. The pressure increases with cross sectional area, and, because straight chain molecules have a smaller cross sectional area, the pressure is therefore reduced and the molecules are pushed into the inner core of the micelle. Also, there is a possibility that the degree of interaction between the hydrophobic chain of the additive and that of the hydrophobic portion of the surfactant is increased. The maximum effect occurs when the chain length of the hydrophobic portion of the surfactant is equal to that of the hydrophobic portion of the additive. The hydrophobic chain length is elongated and solubilization is enhanced.

Organic additives with multiple functional groups that are able to form hydrogen bonds are effective in reducing the CMC. The rationale is that the hydrogen bonding that exists between the polar groups of the additive and those of the water molecule of the surfactant helps to counterbalance the lateral pressure which forces the additive into the interior of the micelle. It can be said that for additives with multiple groups capable of forming hydrogen bonds, the additive will remain in the outer core of the micelle as opposed to additives with only a single group capable of forming a hydrogen bond.[16]

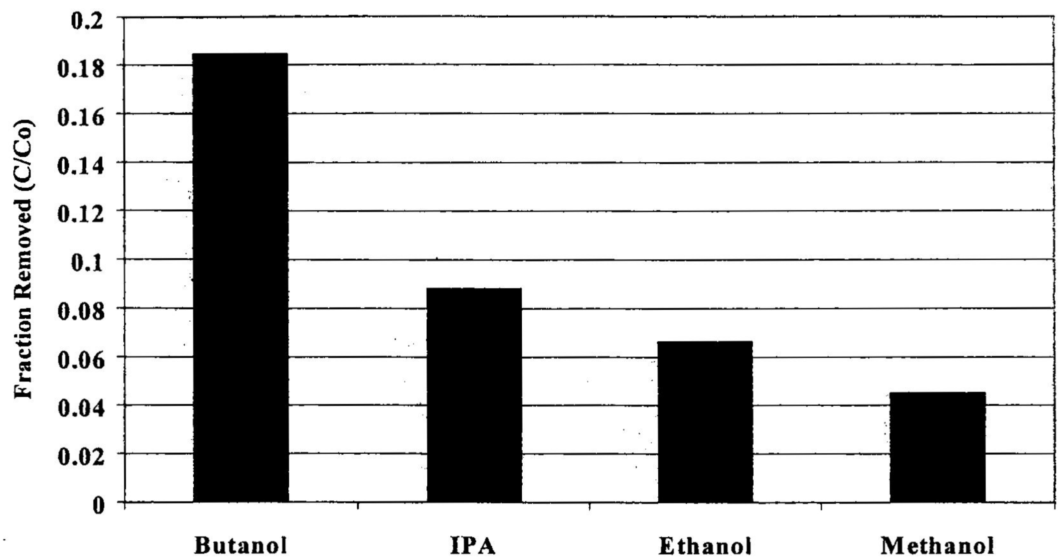


Figure 4.20: PCB Removal Using 0.3 M Alcohol in 0.1 Wt % Witconol SN-70

The addition of organic material, such as alcohols and amines, is capable of producing marked changes in the CMC of surfactants in aqueous solution by being incorporated into the micelles. Because some of these materials may be present as impurities or by products of the manufacture of surfactants, their existence may cause some change in the performance of commercially available surfactants. Therefore, a knowledge of the activity of organic additives in surfactant solutions is of paramount importance, and in this case of practical use. Adsorption of the shorter chain alcohols occurs in the exterior portion of the micelle in close proximity to the water micelle interface. The longer chain alcohols tend to be adsorbed near the outer portion of the micelle. Figure 4.20 shows the fraction of AR 1254 removed from soil laden with 100 mg/kg of the contaminant by extraction with 0.1 wt % Witconol SN-70 containing 0.3 M concentration of various alcohols. In the presence of alcohols, the extraction efficiency of the surfactant was significantly reduced. For alcohols added to a 0.1 wt % (CMC) surfactant solution, the maximum amount of PCBs removed was approximately 0.18 or (18%) of the expected amount.

The order in which the alcohols affected (reduced) extraction efficiency was as follows: butanol <isopropanol (IPA)< ethanol < methanol. The results indicated that the smaller the molecule the greater its effects in reducing surfactant efficiency. A similar trend is observed upon addition of a 0.3 M butanol to 0.25 wt % Witconol SN-70, using the same alcohol strength in a more concentrated surfactant solution. As the carbon chain increases, the less effect the organic additive has on surfactant solubilization. The shorter chain alcohols may be able to increase the CMC because they increase the solubility parameter of the water, thus increasing the solubility of the monomeric form of the surfactant and hence increasing the CMC.[37] More succinctly, the action of the surfactant is based on the reduction of the dielectric constant in the aqueous phase.[38] This would cause mutual repulsion of the ionic heads in the micelle, thus opposing micellization and increasing the CMC.

CHAPTER 5

CONCLUSIONS

5.1 Conclusions

The Savannah River Site soil investigated in this study was determined to be a low cation exchange capacity, low total organic content, and low total surface area sandy soil. PCBs spiked onto the soil was distributed according to particle sizes. The smaller the particle size fraction, the higher the surface area and the higher the PCB loading. Anionic and neutral surfactants and combinations thereof showed various degrees of effectiveness in extracting the PCBs from soils, based on the surfactant type, amount and their critical micelle concentration. The following surfactants were most effective in extracting PCBs from the 100 mg/kg spiked soil: SDS, 1-DPC, Witconol SN-70, and Igepal CA-720. The accurate analysis of PCBs in the surfactant during the screening was hampered by significant matrix interferences caused from the formation of emulsion during the liquid-liquid surfactant hexane extraction process. The use of small amounts of IPA was effective in breaking the emulsion. However, the recovery of PCBs from the surfactant into the hexane extract for analysis varied as the surfactant type and concentrations changed. PCB recoveries from Brij 30, Witcolate D51-51, Triton x-100, and Witcodet increased as the surfactant's concentration increased. The recovery of PCBs from Witconol SN-70 was constant over a range of surfactant concentration investigated.

Based on constant recovery, coupled with the high soil extraction potential it demonstrated, Witconol was chosen as a model surfactant for further soil washing investigation. Witconol had a CMC of 0.05 wt %. The solubility of PCBs in the surfactant was very low below its CMC, but increased with surfactant concentration above the CMC. The surfactant was effective at dissolving PCBs from soil, but its effects were hindered possibly by mass transfer limitations. Using a 5% surfactant solution, the maximum amount extracted from a 100 mg/kg soil can be achieved within 24 h at 25°C. At higher temperatures, 30°C and 40°C, the maximum amount removed was reduced to 50%. This was attributed to disruption of the surfactant micelles at the elevated temperature. Initial modification of pH of the soil-surfactant slurry in PCBs extraction was not very effective, possibly due to the buffering capacity of the soil. The addition of inorganic electrolytes and small molecular weight alcohols at approximately 0.3 M concentration caused a significant reduction in the surfactant extraction efficiency.

More research is needed to investigate the extent to which these findings applies in general to different types and concentration of surfactants.

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